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MONOMOLECULAR FILMS OF MOLECULES WHICH LIE FLAT ON THE SURFACE OF WATER

I. SURFACE PRESSURES AND POTENTIALS OF FILMS OF LONG MOLECULES: POLYMERS OF ω-HYDROXY DECANOIC ACID

A DISSERTATION SUBMITTED TO THE FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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HERMAN ELKAN RIES, JR.

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Monomolecular Films of Molecules Which Lie Flat on the Surface of Water

I. Surface Pressures and Potentials of Films of Long Molecules: Polymers of ω-Hydroxy Decanoic Acid

HERMAN E. RIES, JR., *University of Chicago*
(Received September 3, 1935)

Film pressures and surface potentials have been measured for a series of linear polymers of ω-hydroxy decanoic acid, ranging in molecular weight from 780 to 25,200. The molecules are oriented parallel to the surface. An improved form of the apparatus of Harkins and Fischer was used. The chief modification in the procedure was the use of two radioactive polonium electrodes over the film. The pressure-area relations show that the area per molecule in the condensed films is nearly proportional to the molecular weight and that the compressibility of the films is large. The film density is found to be lowest for the polymers of smallest molecular weight. The films are not very sensitive to changes in hydrogen ion concentration, but on changing from an acid to an alkaline substrate the films in the expanded state give higher molecular areas at given pressures, and the pressures for film collapse are considerably higher. Dimensions of the molecules are calculated and a complete table of mean values is included. The vertical cross section of the molecules varies between 19.4 and 19.9 sq. A or is nearly the same as the horizontal cross section (20.5) of vertically oriented molecules such as stearic acid. Some differences between films with perpendicular orientation to the surface and those with parallel orientation are tabulated. The surface potentials of the polymer films rise to between 400 and 450 mv, although the surface density of the polar groups is only 1/3 to 2/5 that of stearic acid type films, which also give potentials of about 400 mv. The contribution of each polar group is, therefore, considerably greater than that of the dipole of the vertically oriented stearic acid molecule. The surface potential of a condensed film was found to increase about 13 percent less rapidly than the surface density of the dipoles.

I. Introduction

WHILE extensive researches have been carried out with substances whose molecules when in a film on water exhibit an orientation perpendicular, or nearly perpendicular, to the plane of the surface, very little work has been done with molecules which give an orientation parallel to the surface. For this to occur it is only necessary, as pointed out in 1916 by Harkins, Davies and Clark[1] that the polar groups in an organic molecule have a proper symmetrical distribution in the molecule. The best distribution is that of the type exhibited by the linear polymers of ω-hydroxy decanoic acid of the formula $HO[(CH_2)_9COO]_xH$ as supplied to us by Drs. W. H. Carothers, E. O. Kraemer and F. J. van Natta.[2] These polymers, of molecular weights from 780 to 25,200, and values of x from approximately 4 to 148, consist of unbranched chains, and with a polar group at every tenth carbon atom.

It was, therefore, assumed, before the experimental work was begun, that these molecules would lie flat on the surface, and the data obtained in the investigation show that this is true.

II. Filmometer

The apparatus used for this work was an improved form of that of Harkins and Fischer.[3] The changes in the apparatus that seemed to contribute to greater accuracy in the work were chiefly as follows:

(1) Two independent radioactive polonium electrodes were used in such a way as to allow movement in any direction. This made it possible to determine almost simultaneously the potential at two different locations. The second electrode was originally designed to test for leakage past the float, but it was found to be of value when used over the film with the first electrode, since it gives a definite indication of the homogeneity or nonhomogeneity of the film. At the same time it serves as a valuable check on the potential measurements after the film has become uniform.

(2) A suspended carrier was used to raise the entire film balance above the trough, as in the work of Gorter. This arrangement permits sweeping the full length of the tray. If the float is raised and lowered several times during this full length sweeping, the operation amounts to a final washing of the float immediately before the experiment is begun.

(3) Special barriers were constructed for use in sweeping close to the float of the balance. These barriers are so shaped that they may be brought into very close proximity to the float and its delicate gold foils. They are used after the float apparatus has been lowered into place and clamped in position.

(4) The float apparatus is clamped securely to the beveled sides of the trough with a wedge-screw device.

(5) Brass weights or compression springs are used on the glass barrier during the compression of the film to insure a firm contact between the paraffined surfaces of the barrier and the edges of the trough.

Redistilled chloroform was used as the solvent in preparing dilute solutions of the polymers.

III. Pressure-Area Relations

The pressure-area relations of nine linear polymers are given in Fig. 1.

The films are of the "expanded" type at pressures below about 1.3 dynes, and condensed at higher pressures.

The area (a) per molecule in the condensed films is found to be nearly proportional to the molecular weight at any given film pressure. Fig. 2 shows that this is true for the areas extrapolated to zero pressure.

The compressibility of the condensed films is very large, since the value of $[(a_0-a_1)/a_0]/(f_1-f_0)$ lies between 0.040 and 0.053, and is almost independent of molecular size. Similar values for vertically oriented molecules are in general only one-tenth to one-sixtieth as large.

Because of this high compressibility, the accuracy and reproducibility of the work on these films is not expected to be as high as for those which exhibit the other type of orientation,

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[1] Harkins, Davies and Clark, J. Am. Chem. Soc. **39**, 584 (1917).

[2] Kraemer and van Natta, J. Phys. Chem. **36**, 3175 (1932). Carothers and van Natta, J. Am. Chem. Soc. **55**, 4714 (1933).

[3] Harkins and Fischer, J. Chem. Phys. **1**, 852 (1933).

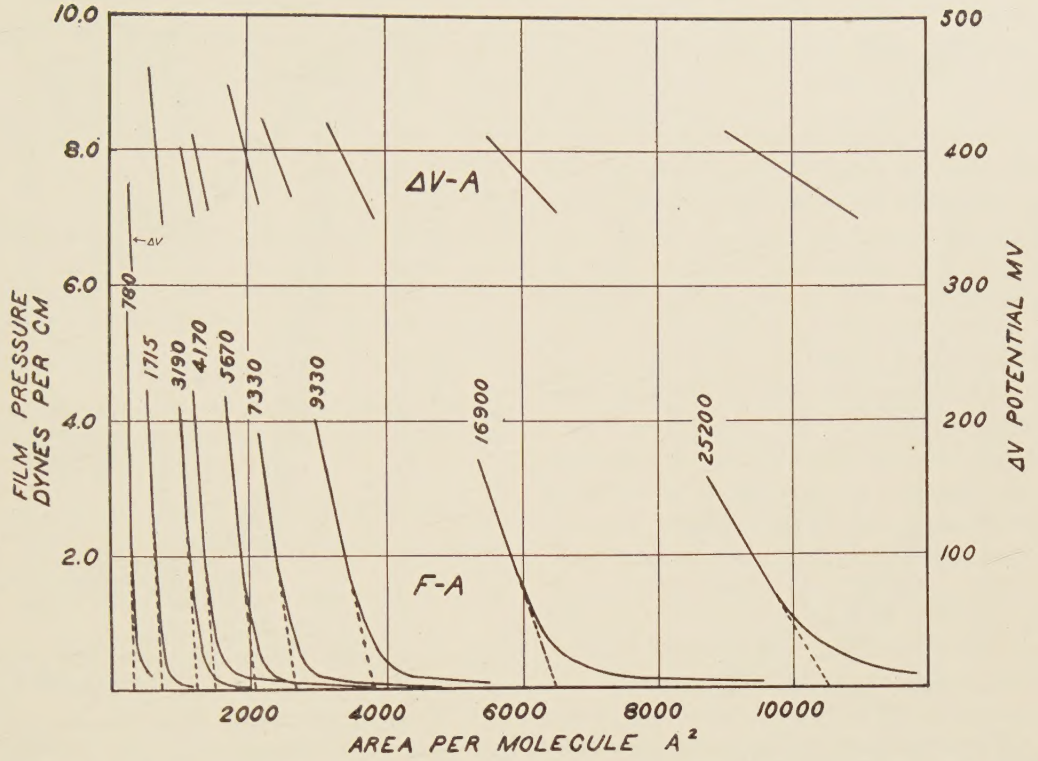

FIG. 1. Exhibits the fundamental relations of films of molecules which lie flat on the surface of water. Film pressure (f) and surface potential relations of linear polymers of molecular weights from 780 to 25,200.

as commonly investigated. However, Figs. 3 to 8, which represent the data, show that when the conditions are identical, a considerable degree of accuracy is attained. It should be noted that the areas are affected by the pH of the solution, especially at low pressures.

While the concentration of material in the film is at any given pressure not highly dependent on molecular size, the lowest density is found for the smallest molecules, those of molecular weight 780, and the highest film density for those of intermediate size (7330). This is shown in Table I.

TABLE I. *Density of films in units of 10^{-8} gram per sq. cm.*

MOLECULAR WEIGHT	DENSITY AT 3 DYNES PER CM PRESSURE	MOLECULAR WEIGHT	DENSITY AT 3 DYNES PER CM PRESSURE
780	4.5	16900	5.1
1715	4.6	5670	5.2
25200	4.7	4170	5.3
9330	4.8	7330	5.4
3190	4.9		

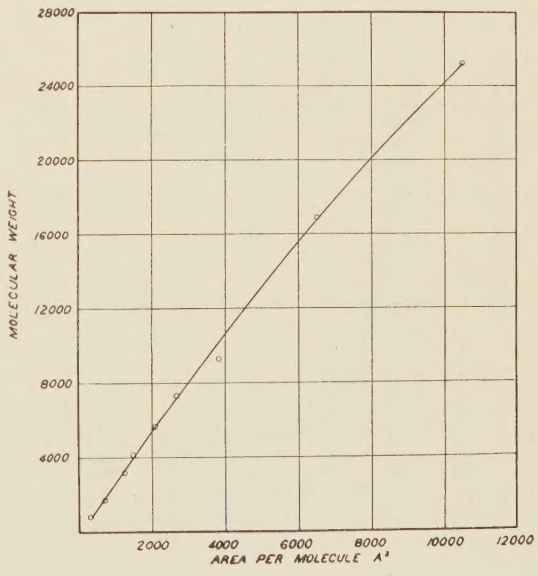

FIG. 2. Exhibits the nearly linear relation between molecular area at zero pressure and the molecular weight of a linear polymer.

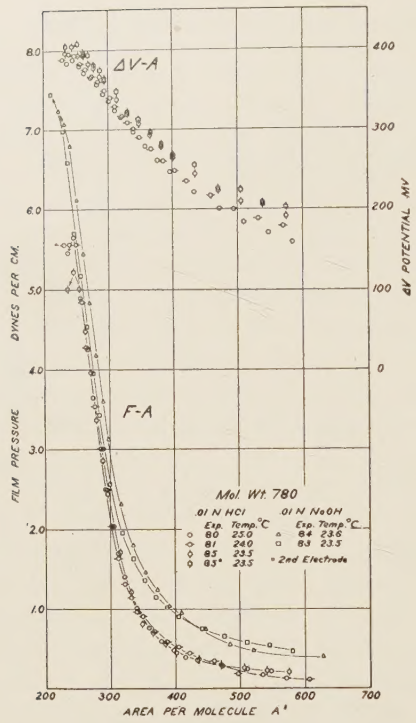

FIG. 3. Film pressure and surface potential relations of the polymer of molecular weight 780 on 0.01 N aqueous solutions of acid and base.

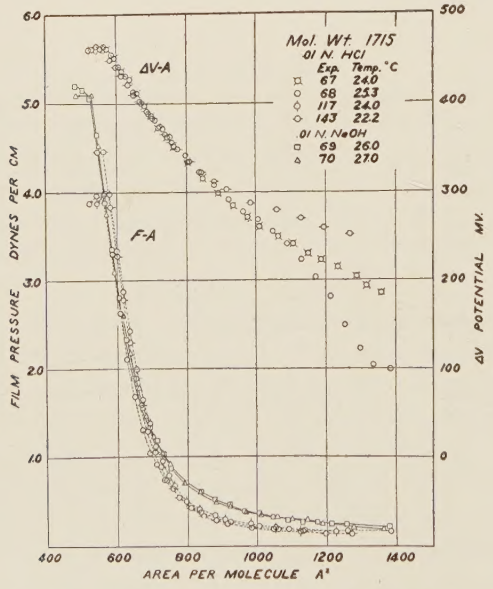

FIG. 4. Film pressure and potential for the polymer of molecular weight 1715.

It may be noted that the pressure-density curves for the condensed films are linear and nearly parallel (Fig. 9).

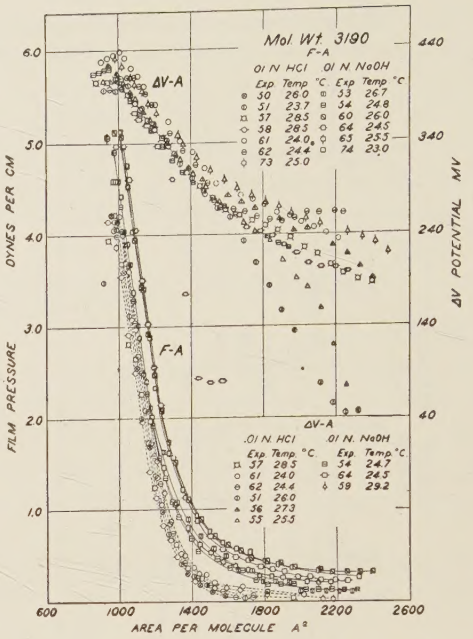

FIG. 5. Polymer of molecular weight 3190. Islands are prominent in the films at areas above 1800 sq. A.

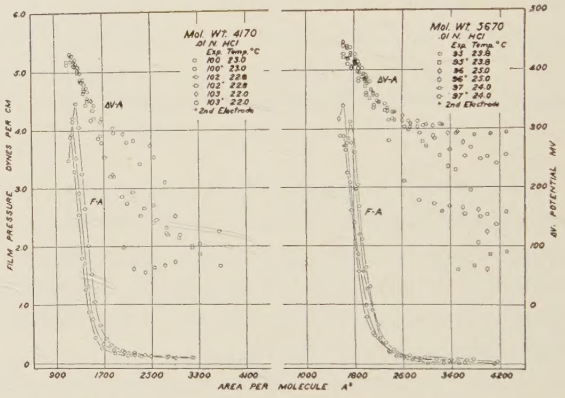

FIG. 6. Polymers of molecular weights 4170 and 5670. Exhibit a marked island effect at higher areas.

IV. EFFECTS OF ACIDS AND BASES

While these films are not extremely sensitive to a variation of the hydrogen ion concentration, two important differences are found.

The molecular area for the expanded film is higher for any given pressure when the aqueous substrate is alkaline with 0.01 molal sodium hydroxide than when acid with 0.01 molal hydrogen chloride.

The pressure of collapse is *much* higher on the alkaline than on the acid solutions: e.g., 7.5 dynes per cm as compared with 5.5 for the

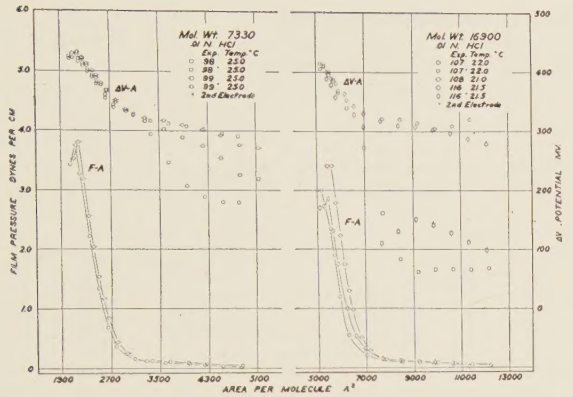

FIG. 7. Polymers of molecular weights 7330 and 16,900. For the latter the potential relations show the island effect at areas above 7000 sq. A.

polymer of M.W. 780; 5 as compared with 4 for M.W. 1715 and 3190; 4 as compared with 3 for M.W. 9330.

V. MOLECULAR DIMENSIONS

The volume of the molecule, as given in Table II, is obtained from the density. The length of the molecule is calculated from the atomic spacing in linear hydrocarbon derivatives as obtained from x-ray investigations. The apparent thickness of the film, columns 9, 10, and 11, is calculated on the basis of a layer of the same density as that of the solid compound. The area per molecule (cols. 5, 6, and 7) is obtained from the experimental values and Avogadro's number.

The width of the molecular space (cols. 12, 13, and 14) is of interest. At the maximum pressure, the film may be slightly folded, so the values at 3 dynes per cm will be considered. At this pressure, the width of the molecular space varies from 4.0 to 4.8A, with a mean value of 4.3. This distance agrees well with that found between linear hydrocarbons in crystals, or with the spacing in liquids, as revealed by x-rays.

If it be assumed that on compressing the film beyond zero extrapolated pressure, the distance between the chains remains constant, the actual distance between carboxyl groups in the same chain will decrease. At zero extrapolated area the average length per chain is 14.7A; at a pressure of three dynes the average distance between carboxyl groups is 12.6A, which amounts to a decrease of 2.1A. This decrease would cause the chain to bow since it is anchored to the surface at both ends by carboxyl groups. However, it is probable that the decrease in distance between adjacent chains is a more major effect than this type of buckling of the molecule.

The most prominent characteristics may be

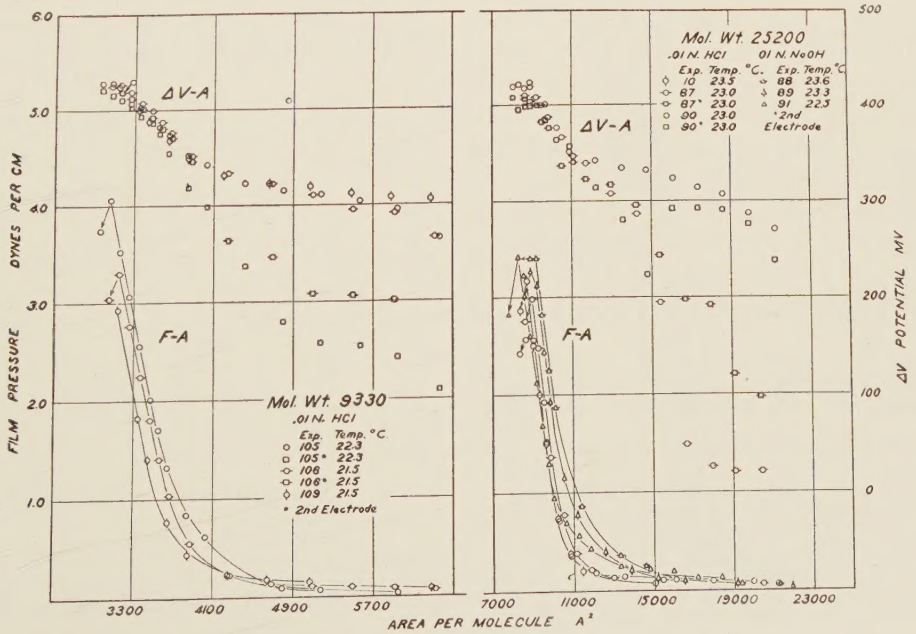

FIG. 8. Polymers of molecular weights 9330 and 25,200.

TABLE II. *Films of polymers of ω-hydroxy decanoic acid on water.*
Mean values at temperatures from 21.5 to 26.0°. Concentration of hydrogen chloride in the water 0.01 *M*
Columns 2 and 3 are taken mostly from the paper of Carothers and van Natta.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
MOL. WT.	DENSITY d^{25}_4	LENGTH OF MOLECULE (A)	VOL. OF MOLECULE (cu. A)	AREA PER MOLECULE AT A FILM PRESSURE $f=0$	$f=3$	$f=$max.	MAXIMUM FORCE f_m	t=THICKNESS OF FILM AT A FILM PRESSURE $f=0$	$f=3.0$	$f=$ max.	d=WIDTH OF MOLECULAR SPACE AT $f=0$	$f=3.0$	$f=$ max.	$t\times d$ MOLECULAR CROSS SECT. AT 3 DYNES (sq. A)	COMPRESSIBILITY AT $f=0$
780	1.0957	60	1170	330	290	246	5.7	3.6	4.0	4.8	5.5	4.8	4.1	19.5	0.040
1715	1.0935	133	2590	700	604	556	4.5	3.7	4.3	4.7	5.3	4.5	4.2	19.4	.046
3190	1.0877	248	4840	1260	1080	970	4.2	3.9	4.5	5.0	5.1	4.4	3.9	19.6	.048
4170	1.0814	324	6360	1490	1300	1130	4.5	4.3	4.9	5.6	4.6	4.0	3.5	19.6	.043
5670	1.0751	440	8700	2050	1800	1688	4.4	4.2	4.8	5.2	4.7	4.1	3.8	19.7	.041
7330	1.0715	570	11330	2670	2277	2180	3.8	4.2	5.0	5.2	4.7	4.0	3.8	19.9	.049
9330	1.0668	730	14450	3800	3200	3000	4.0	3.8	4.5	4.8	5.2	4.4	4.1	19.8	.053
16900	1.0627	1320	26200	6440	5510	5270	3.4	4.1	4.8	5.0	4.9	4.2	4.0	19.9	.048
25200	1.0621	1970	39100	10430	8800	8700	3.2	3.8	4.4	4.5	5.3	4.5	4.4	19.9	.052

listed for a pressure of 3 dynes per cm unless otherwise stated,

Thickness of films from 4.0 to 5.0A.

Distance between centers of adjacent chains 4.0 to 4.8A. Apparent vertical cross section of molecule 19.4 to 19.9 sq. A, or nearly the same as the horizontal cross section (20.5) of molecules, such as stearic acid, oriented vertically. The area (a) per molecule in condensed films is nearly proportional to the molecular weight at any given film pressure (f).

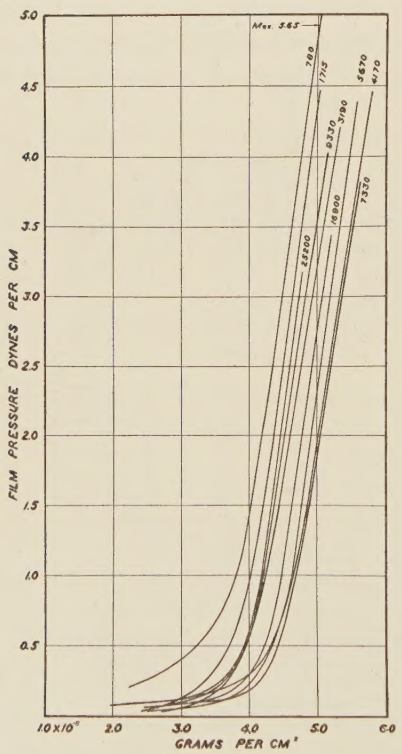

FIG. 9. Density of the films in grams per sq. cm$\times 10^{-8}$ as a function of the molecular weight and of the film pressure.

The molecular area of the compound of molecular weight 25,200 is 10,400 sq. A for zero pressure, or 8800 sq. A at 3 dynes per cm pressure. This is the largest area thus far found for any molecule.

At a pressure of 3 dynes per cm, the area per group of 10 carbon atoms $(CH_2)_9COO$ is a maximum of 65 for M.W. 780, a minimum of 53 for M.W. 4170 and 7330, and rises to 59 for 25,200 (Fig. 10).

VI. ORIENTATION OF THE MOLECULES

That the molecules in these films are oriented parallel to the plane of the surface is shown by the thinness of the condensed films, by the fact that the molecular area is proportional very

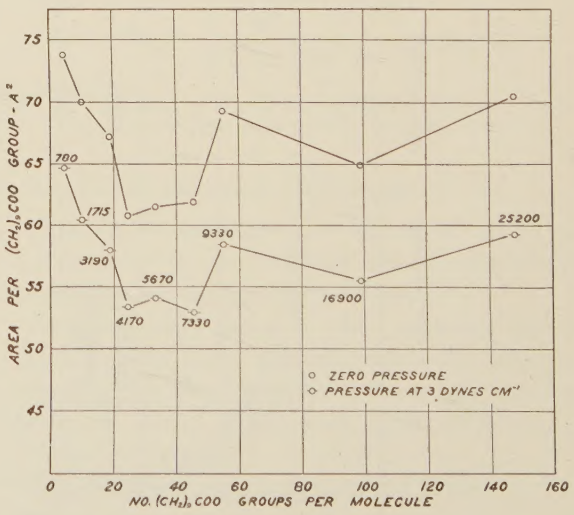

FIG. 10. Area per unit group $[(CH_2)_9COO]$ as a function of the number of unit groups in the molecule at a pressure of 3 dynes per cm and of zero dynes (extrapolated value).

TABLE III. *Properties of films with different orientations of the molecule.*

LONG AXIS VERTICAL	LONG AXIS HORIZONTAL
Molecular area independent of length	Molecular area increases with length
Withstand high pressures (to the order of 50 dynes per cm)	Collapse at low pressures (2 to 10 dynes)
Surface potential increases with length of molecules up to 18 carbon atoms	Surface potentials of the same order for long and short molecules
Compressibility decreases with increasing length of chain	Compressibility high and independent of length of molecules

nearly to the molecular weight, by the independence of the surface potential and the molecular weight, and by the agreement between the width of the molecular space, calculated on the hypothesis that the molecules lie flat and the molecular distances derived from x-ray measurements.

The differences in the properties exhibited by films with perpendicular and parallel orientations to the plane of the surface, are listed in Table III.

VII. SURFACE CONTACT POTENTIALS*

The Righi-Kelvin method for the determination of contact potentials of metals was found by Guyot and by Frumkin to give a contact potential between a metal and the surface of an aqueous solution. While this method did not give consistent results, it was suggested to Frumkin by Harkins that the difficulty did not lie in the method for the determination of the potential, but to variations in the film itself. The use of a combined film pressure apparatus and movable polonium coated electrodes has, as used by various investigators, shown this to be true.

Although the condensed films of the polymers of ω-hydroxy decanoic acid are very thin (*ca.* 4.5A) the surface potentials rise to between 400 and 450 mv, which is as high as for a very thick film of an acid of the type of stearic acid. Stearic acid itself gives about 400 mv.

The surface potential is practically independent of the length of the molecule, while with a perpendicular orientation it increases with the length of the molecule.

The surface potential (ΔV) of any one of the condensed films increases about 13 percent less rapidly than the surface density of the film. Thus the surface potential seems to increase with and nearly as the number of polar groups per unit area. However, the mutual effect of the dipoles is such as to decrease the potential.

At low pressures the expanded films become nonhomogeneous, since the surface potential varies with the location on the surface. This island effect is much more prominent for polymers of high than for those of low molecular weight.

While the number of dipoles in the surface is for the highly compressed film only 1/3 to 2/5 as great as for condensed films of stearic or palmitic acid, the surface potential is as high as that for stearic acid and higher than that for palmitic acid.

It is, therefore, obvious that the surface potential is not proportional to the number of dipoles. At the water surface the COO group might have a higher moment than the COOH group, but it is not improbable that the explanation lies in the dipoles of the water molecules.

However, since considerable work on the problem of the surface potential is in progress in this and in other laboratories, a more general discussion of the factors involved will be left to a later paper.

This work was begun by Dr. Earl K. Fischer under a grant from the Chemical Foundation.

* *Fundamental Papers on Contact Potentials and Papers on Surface Potentials*

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